

different orders should show it, as the measurement of say 10 orders simultaneously existing provides us with a frequency range of ν to 10ν .

¹ L. Brillouin, *Ann. phys.*, **17**, 88 (1922).

² A. Einstein, *Ann. Phys.*, **33**, 1275 (1910).

³ Gross, *Zeit. Phys.*, **63**, 685 (1930); *Naturwiss.*, **18**, 718 (1930); *Nature*, **126**, 201, 400, 603 (1930).

⁴ Meyer and Ramon, *Phys. Zeitschr.*, **33**, 270 (1932).

THE ADDITIVITY OF THE ENERGIES OF NORMAL COVALENT BONDS*

BY LINUS PAULING AND DON M. YOST

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated May 9, 1932

The chemical bond between two identical atoms, as in the molecules H_2 , Cl_2 , etc., may be considered as an example of a normal covalent bond, involving an electron pair shared by the two atoms. The wave function representing this bond cannot necessarily be closely approximated by a function of the Heitler-London type, with the electrons staying on different atoms, but may contain ionic terms, corresponding to the two electrons of the bond on the same atom, the term representing the configuration A^+A^- occurring, of course, with the same coefficient as that for A^-A^+ . The contribution of these ionic terms to the wave function for the normal state of the hydrogen molecule has been discussed by Slater.¹

In the wave function representing the bond between unlike atoms A and B , the ionic terms A^+B^- and A^-B^+ will occur with the same coefficient, of the order of magnitude of those for $A:A$ and $B:B$, if the two atoms have the same degree of electronegativity. We propose to call such a function a normal covalent bond wave function, and the bond a normal covalent bond; and to make the postulate that *the energies of normal covalent bonds are additive*, that is, $A:B = \frac{1}{2}(A:A + B:B)$, where the symbols $A:B$, etc., mean the energies of the normal covalent bonds. This postulate requires that the energy change for a reaction such as $\frac{1}{2}A_2 + \frac{1}{2}B_2 = AB$ involving only normal covalent substances with single bonds be zero. The energy of the normal covalent bond $A:B$ would be given by the integral $\int \psi^* H \psi d\tau$, with ψ the normalized normal covalent wave function. Inasmuch as the energy integral for any wave function for a system must be equal to or greater than the energy of the lowest state of the system, the energy of the actual bond between A and B will either be equal to that for a normal covalent bond $A:B$, or, in case the

bond has ionic character A^+B^- or A^-B^+ in excess of that included in the normal covalent bond, will be greater than this value. Hence, if our postulate is true, actual bond energies will not show negative deviations from additivity; the difference Δ between the actual bond energy and the energy predicted for a normal covalent bond must be zero or positive, and the greater the ionic contribution to the bond, the greater will be the value of Δ .

In Table 1 are given bond energies for hydrogen and the halogens, and their binary compounds, the hydrogen halides and the halogen halides, together with the deviations from additivity. The values of Δ are usually known more accurately than the bond energies themselves because they can be directly measured as heats of reaction. It is seen that the Δ 's

TABLE 1

Bond energy	H:H	F:F	Cl:Cl	Br:Br	I:I
	4.44	2.80	2.468	1.962 ^a	1.535 v. e. ^b
		HF	HCl	HBr	HI
Actual bond energy		6.39	4.38	3.74	3.07
Predicted from additivity		3.62	3.45	3.20	2.99
Δ		2.77 ^c	0.93	0.54	0.08
		ClF	BrCl	IBr	ICl
Actual bond energy		3.82	2.231	1.801	2.143
Predicted from additivity		2.63	2.215	1.748	2.001
Δ		1.19 ^c	0.016 ^d	0.053 ^e	0.142 ^f

^a W. G. Brown, *Phys. Rev.*, **38**, 1179 (1931).

^b W. G. Brown, *ibid.*, **38**, 709 (1931).

^c O. Ruff, *Z. anorg. Chem.*, **198**, 375 (1931).

^d Calculated from unpublished and not final results of Don M. Yost and P. G. Murdoch.

^e J. McMorris and Don M. Yost, *J. Am. Chem. Soc.*, **53**, 2625 (1931); R. M. Badger and Don M. Yost, *Phys. Rev.*, **37**, 1548 (1931).

^f J. McMorris and Don M. Yost, to appear in *J. Am. Chem. Soc.* for June, 1932; also W. G. Brown, private communication.

are positive for all of these compounds, which provides strong support for our postulate. Moreover, the values are in agreement with previously formed conceptions of the nature of the bonds in these molecules. A recent discussion² of energy curves has shown HF to be largely ionic rather than covalent, while HCl, HBr and HI are mainly covalent, with a small amount of ionic character, decreasing in this order to nearly zero for HI. For HF Δ (= 2.79 v. e.) is nearly as large as the total energy of the normal covalent bond, showing the great influence of the ionic structure H^+F^- . In HCl and HBr the ionic character of the bonds, while much less than for HF, is shown to be important by the values 0.93 and 0.54 v. e. for Δ . HI, with Δ only 3% of the total bond energy, approaches closely the normal covalent type.

The compound BrCl approaches the normal covalent type still more

closely, with a deviation from additivity of less than 1%. The values of Δ for IBr and ICl are also small, but that for ClF is even larger than for HCl, showing that chlorine fluoride is more ionic in character than hydrogen chloride. Chlorine, bromine and iodine do not differ greatly in electronegativity, chlorine and bromine being most similar in this as in other respects (for example, in size, the ionic radii being 1.36 Å for F⁻, 1.81 for Cl⁻, 1.96 for Br⁻ and 2.16 for I⁻). But fluorine is very much more electronegative than the other halogens, and deserves to be classed by itself as a superhalogen.

It may be mentioned that the property of electronegativity discussed here is closely related to the electronegativity of the chemist, and has little relation to the electron affinity of gaseous atoms.

We may also test the additivity postulate with compounds of a much different type, involving the alkali metals. It is seen from Table 2 that additivity holds to within the experimental error for the molecules KNa and LiH.

TABLE 2

	Li:Li	Na:Na	K:K
Bond energy	1.14 ^a	0.76 ± 0.02	0.51 ± 0.02 v. e.
		KNa	LiH
Actual bond energy		0.62 ± 0.05	2.6 ± 0.2 v. e.
Predicted from additivity		0.64	2.79

^a F. W. Loomis and R. E. Nusbaum, *Phys. Rev.*, **38**, 1447 (1931).

The alkali halide molecules are known to be mainly ionic. The large values of Δ , some of which are given in Table 3, are in agreement with this.

TABLE 3

	KCl	KBr	KI
Actual bond energy	4.5	3.9	3.25 v. e.
Predicted from additivity	1.53	1.24	1.03
Δ	3.0	2.7	2.22

We recognize that the energies of bonds depend on a great many factors, and that additivity of the energies of normal covalent bonds has no rigorous theoretical justification and cannot be expected to hold in all cases; but we feel that the empirical evidence shows that for a number of compounds of varying types the rule is well satisfied, and we believe that it may be usefully applied in the discussion of the nature of the chemical bond, in particular as a criterion for determining the approximation of a bond to a normal covalent bond and as a means of mapping atoms along the scale of electronegativity.

* Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 315.

¹ J. C. Slater, *Phys. Rev.*, **35**, 509 (1930).

² Linus Pauling, *J. Am. Chem. Soc.*, **54**, 988 (1932).